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**LOS ALAMOS NATIONAL LABORATORY
CARLSBAD OPERATIONS**

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**Technology Applicable to
Remote Hazardous Constituents and Waste Stream Grouping**

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ACRONYMS AND ABBREVIATIONS

| | |
|---------|---|
| AES | - atomic emission spectroscopy |
| AK | - acceptable knowledge |
| ARP | - Accelerated Retrieval Project |
| ATR | - attenuated total reflectance |
| cm | - centimeter |
| CR | - Conventional Raman |
| DPS | - drum packaging station |
| DWT | - (Los Alamos National Laboratory) Difficult Waste Team |
| FTIR | - Fourier transform infrared (spectroscopy) |
| g | - gram |
| Hz | - Hertz |
| ICP | - Idaho Cleanup project |
| IDC | - item description code |
| INL | - Idaho National Laboratory |
| IR | - infrared |
| LANL | - Los Alamos National Laboratory |
| LANL-CO | - Los Alamos National Laboratory – Carlsbad Operation |
| LIBS | - laser induced breakdown spectroscopy |
| LOD | - limit of detection |
| lbs | - pounds |
| mJ | - millijoule |
| µm | - micrometer / micron |
| nm | - nanometer |
| ns | - nanosecond |
| PPE | - personal protective equipment |
| ppm | - parts per million |
| RCRA | - Resource Conservation and Recovery Act |
| s | - second |
| SME | - subject matter expert |
| SORS | - Spatially Offset Raman Spectroscopy |
| SRP | - Sludge Repackage Project |
| TRU | - transuranic |
| USB | - universal serial bus |
| UV | - ultraviolet |
| VE | - visual examination |
| WAC | - Waste Acceptance Criteria |
| WIPP | - Waste Isolation Pilot Plant |
| wt. % | - weight percent |
| XRF | - x-ray fluorescence |

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Technology Applicable to Remote Hazardous Constituents and Waste Stream Grouping

1. BACKGROUND

Originally, Rocky Flats transuranic (TRU) waste was managed from waste streams that were composed of similar chemical constituents and were generated from identical processes. Early waste processing at Idaho National Laboratory (INL) maintained the Rocky Flats record until INL began generating their own item description codes (IDCs). Ultimately TRU waste management at INL was driven to combine wastes from all IDCs that were assigned by Rocky Flats to a summary category group regardless of whether the chemical constituents in the waste were known or not. At this point, the Waste Isolation Pilot Plant (WIPP) certified program requirements to process the TRU waste according to waste streams was nearly eliminated.

In April 2018, operations in the Sludge Repackage Project (SRP) area were halted by a radiological materials release accident in which drums containing waste experienced a loss of containment after over-pressurization occurred. Four SRP drums, repackaged in the Accelerated Retrieval Project (ARP) V area, had an adverse, delayed chemical reaction event occur when prohibited materials from one container were mixed with chemically-incompatible materials from other containers in the repackaging process. This incident was the direct result of processing unknowns under a protocol where the components of the waste were added to incompatible materials resulting in a run-away reaction.

After a Difficult Waste Team (DWT) and Los Alamos National Laboratory – Carlsbad Operations (LANL-CO) subject matter expert (SME) visit in September 2019, it was determined by the team that all of the work observed on the September visit was performed upstream of the certified program and that the Visual Examination (VE) and other methods typically used by the certified program were being used for Acceptable Knowledge (AK) augmentation. This augmentation was needed in order to determine what the constituents in the waste might be, and is based primarily on collections of VE results. The waste at INL that is being processed in what is considered to be the Priority 2 (yellow) and Priority 3 (red) lists either needs AK to be completed before certified characterization can occur or is waiting to be processed because the waste has been mixed with unknown wastes resulting in a lack of information that could have impact of the ability to certify and ship the waste to the WIPP.

2. PROBLEM STATEMENT

In order to be compliant with the WIPP Hazardous Waste Permit Appendix C, INL must have a means to distinguish ways to collect containers of TRU waste into waste streams based on like constituents in the waste and use these waste streams as the basis of characterization and certification for shipment. The identification and assignment of containers in waste stream is required regardless of IDC assignment. Past waste management practices used by multiple INL contractors have created a large volume of TRU waste that is not characterized, because it has been mixed with unknown waste. Resource Conservation and Recovery Act (RCRA) and WIPP compliant shipments cannot be certified with unknown waste. Therefore, waste must be characterized in order for an accurate and compliant waste description to be documented in the AK record used to certify the waste. Remote methods can be used to sort waste into waste streams and screen for metals that may be problematic such as beryllium and uranium to address chemical safety concerns where chemical data is lacking.

3. LABORATORY METHODS ADAPTED TO THE FIELD

Common laboratory methods that have been adapted to spectroscopic field techniques include infrared (IR) and Raman spectroscopic methods that are capable of detection of vibrational motion in molecules and atomic emission spectroscopy (AES) which detects light emission after a metal or atomic species is excited by an energy source such as a torch or laser as in the case of laser induced breakdown spectroscopy (LIBS).

IR spectroscopy is based on the absorption of IR radiation by molecules. When an infrared frequency is absorbed by a molecule at the natural frequency of vibration of a particular bond between atoms in a molecule, the resulting frequency of absorbed IR energy can be used to determine molecular structure based on functional groups in the molecule. These functional groups within pure samples may provide an IR spectrum that is unique to that molecular species and can be called a fingerprint of that molecule. The same fingerprint concept can be used for a group of chemicals that may be present in a waste stream. Fourier transform infrared (FTIR) spectroscopy is an IR spectroscopy that provides higher resolution and decreased noise, applying Fourier transformations.

Raman spectroscopy is a laser light scattering technique that does not depend on a specific frequency to provide a unique or characteristic peak of interest. When light interacts with a molecule, the light may leave behind an amount of energy that is equal to the natural vibration in a molecular bond or a set of bonds in a functional group. When this happens the laser frequency that is returned is shifted by the amount of energy imparted to the molecule and can be used to detect the finger print of the

material of interest. Just like IR, the spectrum generated can be used to speciate a pure chemical or a group of chemicals as long as functional groups are present.

AES requires high power sources to transform samples into an energetic form that releases light when it loses energy. In field applications energetic bombardment of material of interest from a highly focused laser vaporizes a small fraction of the material creating a plasma. This plasma consists of heated atoms that have been stripped of their electrons and the electrons that have been stripped from them. When the plasma cools (within microseconds) the electrons recombine with the energized atoms and in the process emit light in the ultraviolet region, and optical regions of the electromagnetic spectrum that is specific for the material interrogated. LIBS is capable of analyzing any element on the periodic table which makes it more suitable to a wider range of materials than x-ray fluorescence (XRF) another field method that uses x-rays to elevate electrons to a more excited state within atomic species and relies on the ability of the atomic species to absorb x-rays. Lighter atomic species (such as beryllium) are not amenable to x-ray excitation.

For this report we mainly considered hand-held in-field instruments that have the capacity to be operated within a glovebox. As such the instruments need to be light weight and have small footprints. Operation of the instruments needs to be simple enough that it can be accomplished with the limited dexterity caused by thick glovebox sleeves. Many in-field instruments are designed around identifying known materials from a built in library, however since waste cleanup operations potentially deal with unknown mixtures, the resulting data will need to be reviewed for identification. Options for data transfer must also be considered so that data can be handled outside of the glovebox. Some form of wireless transfer such as Bluetooth or Wi-Fi should be considered with workstations that can be set up outside of the glovebox. However, this is not an absolute requirement as a small computer could be placed in the glovebox and then employ a wireless display adaptor and wireless mouse and keyboard for operation outside the glovebox. There are many options that can be implemented.

4. RESULTS AND PROPOSED USES THAT MAY BENEFIT IDAHO

Multiple vendors were sent standard material, some spiked with magnesium nitrate hexahydrate (see descriptions in attachments A and B). The results obtained indicate that FTIR can be used to provide fingerprint capability for constituents in waste streams such that waste streams may be sorted according to known chemical constituents. Raman spectroscopy is a tool that can be used for determination of nitrate and possibly other oxidizing chemicals in solids and has particular applicability in solutions that may be useful when unknown liquids are encountered in the ARP and SRP. Beryllium and uranium can be simultaneously analyzed using LIBS so that particular waste streams that contain both constituents can be screened during processing. In addition, LIBS can be used to provide the known metal constituents that

may be present in the waste encountered. Examples of each application are provided in summary below. Additional detail can be obtained in attachments A and B. Figure 1 is an example of the type of spectrum that can provide an FTIR fingerprint. It contains an overlay of FTIR spectra of pure magnesium nitrate hexahydrate with that of a surrogate waste sample spiked with 10 wt. % magnesium nitrate hexahydrate. The sharp peak seen around 1650 cm^{-1} is characteristic of the nitrate ion and it is seen in the magnesium nitrate hexahydrate spectra as well as in the spectra of Surrogate A. This shows that FTIR can be used to obtain chemical information on a sample while also providing a unique spectrum that can be used to group together unknown samples.

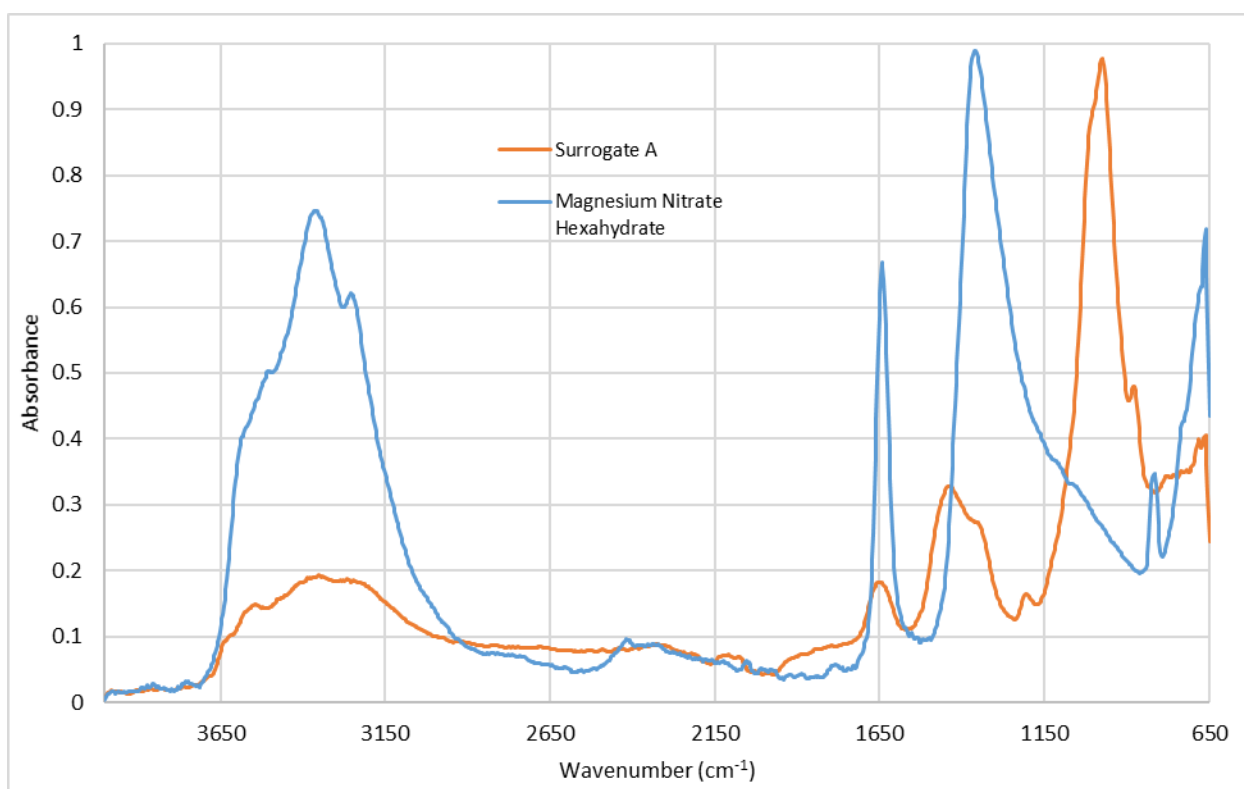


Figure 1: FTIR spectra overlay of Surrogate A and magnesium nitrate hexahydrate.

Figure 2 shows the resulting Raman spectra of magnesium nitrate hexahydrate and Surrogate A. The characteristic peak for nitrate appears in the range of $1000\text{--}1100\text{ cm}^{-1}$ and can be seen in both samples. It shows that Raman may be used for the determination of nitrate and other molecular oxidizing chemical species that are expected to be seen in specific waste streams. Raman spectroscopy can also be used to determine the presence of nitrate ion and other oxidizing chemical ions in solution, and will be of particular use when needing to identify unknown liquids.

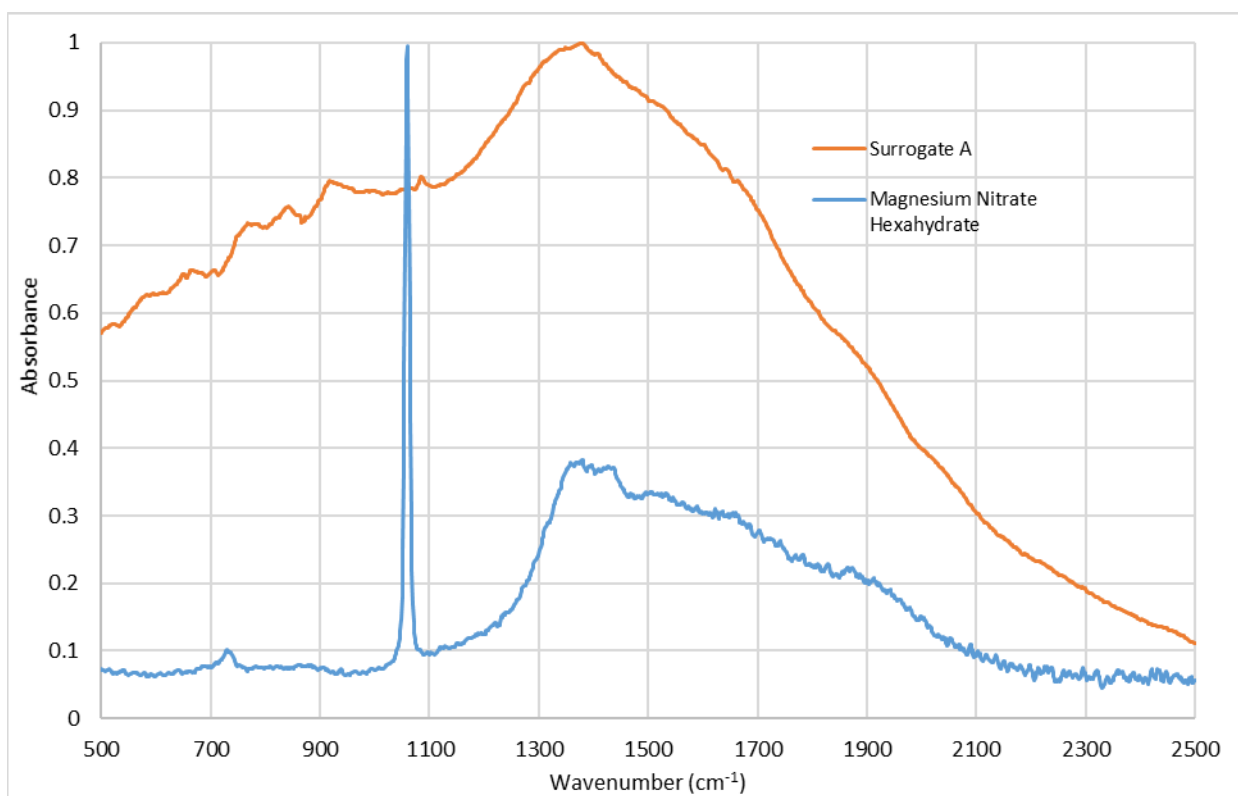


Figure 2: Raman spectra Overlay of Surrogate A and magnesium nitrate hexahydrate.

Figure 3 shows atomic spectra that highlight the capability of beryllium detection in soil and sludge standard matrices using a handheld LIBS instrument. The sewage sludge is composed of several metals (see discussion in attachment B) and includes beryllium at 0.003 wt. %. Uranium is not included in this sample but has been analyzed in loose powder form by LANL, indicating that metal results are possible using un-pressed powders and dirt (see attachment B).

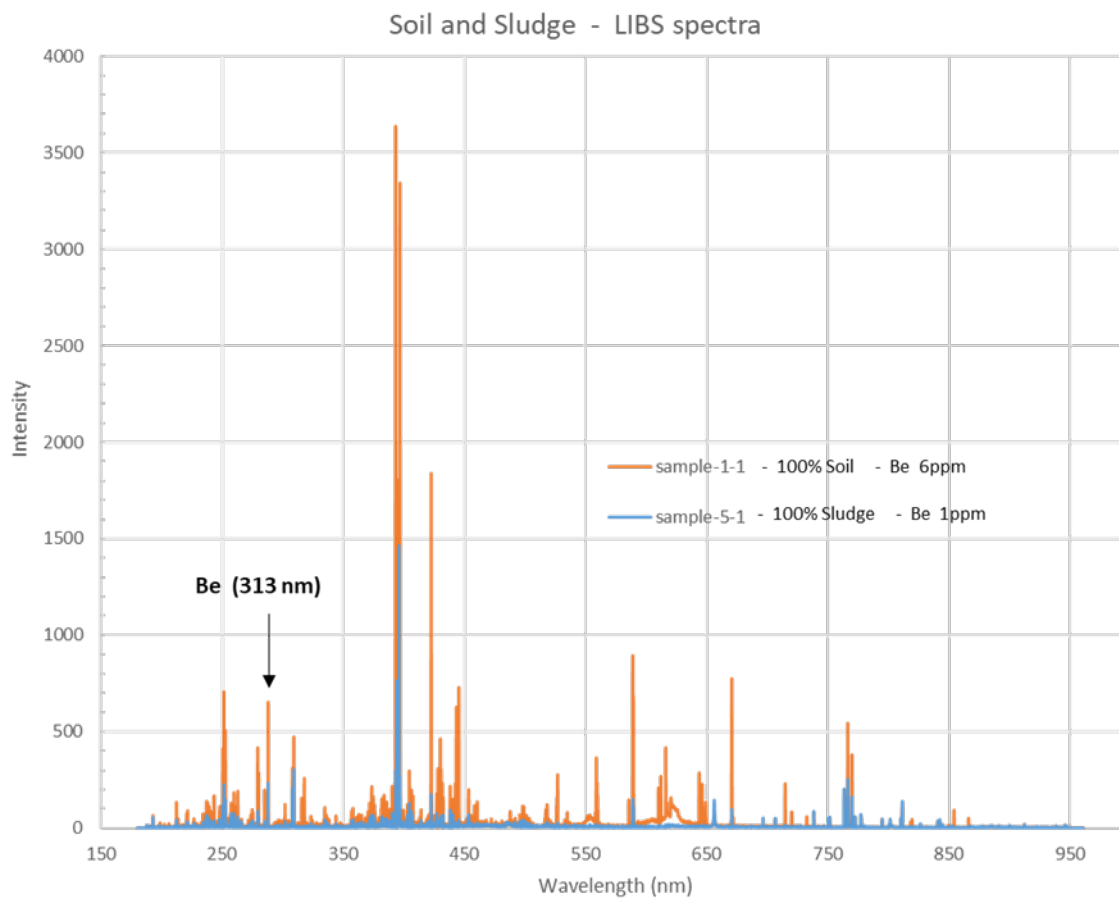


Figure 3: LIBS spectra of pelletized standard soil and sludge.

Attachment A: Vibrational Spectroscopy

Derek Brigham (LANL DWT)

A. Vibrational Spectroscopy

A1. Infrared Spectroscopy

Infrared spectroscopy is a common and widely used spectroscopic technique. Beginning in the 1950's, the use of IR spectroscopy did not become widespread until Fourier Transformations were applied to the technique in the 1960's, providing higher resolution and decreased noise. Fourier Transform Infrared (FTIR) Spectroscopy provides a means of rapidly scanning samples and obtaining a great deal of structural information from a molecule. A basic FTIR spectrometer (Figure 4) consists of a source, interferometer, detector, analog to digital convertor, and a computer. The source generates the IR radiation which is then directed to the interferometer which then redirects the light to the sample and then on to the detector. The detected signal is digitized and then processed by the computer to produce the IR spectrum.

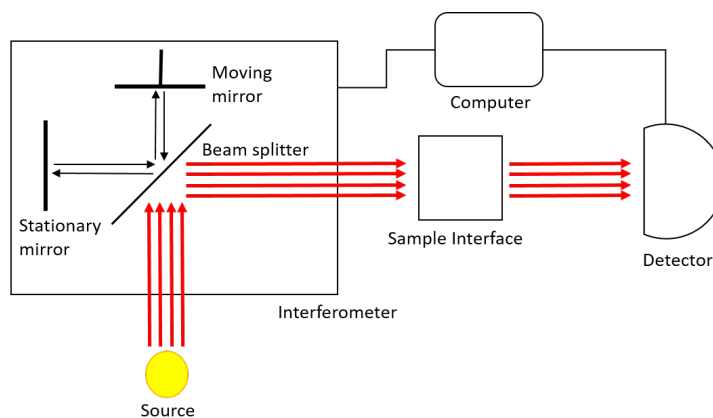


Figure 4: FTIR spectrometer block diagram.

IR spectra are generated from the absorption of infrared light by a molecule. For a molecule to be IR active there must be chemical bonds present that will undergo a change in the dipole moment of the bond when exposed to IR radiation. The absorption of the IR radiation causes the bond to stretch and/or bend leading to the change in the dipole moment. This effect more readily occurs when there is already a permanent dipole moment

in the bond. When a molecular species has a permanent dipole, IR spectroscopy is an excellent means for detecting organic functional groups as different types of chemical bonds absorb IR radiation at specific frequencies (Table 1). This provides a powerful method for identifying compounds as different molecules will have a unique IR “fingerprint”. While the entire IR spectrum is useful for identifying compounds, the region of the IR spectrum from 1500 to 500 cm^{-1} is particularly useful due to the large number of absorption bands present there and is often referred to as the fingerprint region.

A2.Raman Spectroscopy

When light at a specific wavelength interacts with molecular bonds, the light may be absorbed by the bond or scattered by it. When light is scattered it can be done through elastic scattering, where there is no energy exchange between the light and the bond, or inelastic scattering, where there is some exchange of energy between the incident light and the bond. Inelastic scattering causes the frequency of the scattered light to be altered from the incident light. This change in frequency will be specific to the incident light and the type of bond it interacted with. The scattered light can be collected by a detector to generate what is known as the Raman spectrum. The spectrum that is generated can provide chemical and structural information about a molecule and its environment.

In all cases where Raman spectroscopy is performed, a laser is used as an excitation source at the specified wavelength. This laser beam is focused through filters and mirrors to deliver light at a specific frequency to the sample. The scattered light is then focused into a spectrometer or grating that breaks down the resultant light into characteristic frequencies and intensity that provide a Raman spectrum as shown in Figure 5.

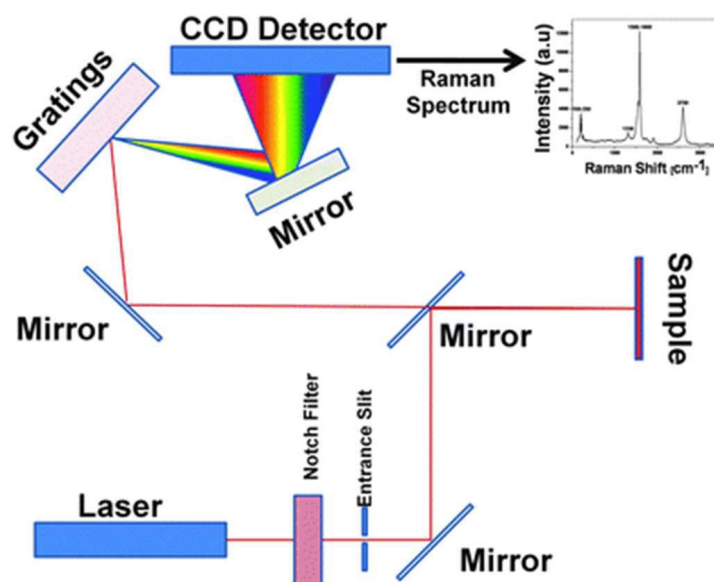


Figure 5: Example of a Raman Spectrometer [2].

Table 1: Functional group IR absorption bands [1].

| Compound Class | Group | Absorption (cm ⁻¹) | Appearance |
|-------------------------|------------------|--------------------------------|---------------|
| acid halide | C=O stretching | 1815-1785 | strong |
| alcohols | O-H stretching | 3700-3584 | medium, sharp |
| | O-H stretching | 3550-3200 | strong, broad |
| | O-H bending | 1420-1330 | medium |
| aldehyde | C-H stretching | 2830-2695 | medium |
| | C=O stretching | 1740-1720 | strong |
| | C-H bending | 1390-1380 | medium |
| aliphatic ether | C-O stretching | 1150-1085 | strong |
| aliphatic ketone | C=O stretching | 1725-1705 | strong |
| aliphatic primary amine | N-H stretching | 3400-3300 | medium |
| alkane | C-H stretching | 3000-2840 | medium |
| | C-H bending | 1450 | medium |
| | C=C stretching | 1648-1638 | strong |
| | C=C bending | 730-665 | strong |
| alkyl aryl ether | C-O stretching | 1275-1200 | strong |
| alkyne | C-H stretching | 3333-3267 | strong, sharp |
| | C≡C stretching | 2260-2190 | weak |
| | C≡C stretching | 2140-2100 | weak |
| amine | N-H bending | 1650-1580 | medium |
| | C-N stretching | 1250-1020 | medium |
| carboxylic acid | O-H stretching | 3300-2500 | strong, broad |
| | C=O stretching | 1760 | strong |
| | C=O stretching | 1720-1706 | strong |
| | O-H bending | 1440-1395 | medium |
| ester | C-O stretching | 1210-1163 | strong |
| esters | C=O stretching | 1750-1735 | strong |
| fluoro compound | C-F stretching | 1400-1000 | strong |
| halo compound | C-Cl stretching | 850-550 | strong |
| | C-Br stretching | 690-515 | strong |
| | C-I stretching | 600-500 | strong |
| isocyanate | N=C=O stretching | 2275-2250 | strong, broad |
| isothiocyanate | N=C=S stretching | 2140-1990 | strong |
| nitro compound | N-O stretching | 1550-1500 | strong |
| phenol | O-H bending | 1390-1310 | medium |
| sulfate | S=O stretching | 1415-1380 | strong |

Figure 6 shows a spectrum of a supernate from a Hanford waste tank (Tank U-108). This spectrum illustrates how oxyanions appear in supernate taken from Hanford tank samples that contain multiple ionic species and suspended particulates from evaporate salts

generated at Hanford's U-plant. This particular spectrum was obtained with a fiber optic probe using a near IR laser for excitation. Note that there are no peaks present for the silica that is part of the fiber optic. This is because silica can be identified in IR but is not Raman active. Nitrate, nitrite, and sulfate ions can be detected at 0.3 wt. % and higher concentrations. Nitrate ion is present in this waste at 17.4 wt. % and nitrite was determined to be at 13.1 wt. %. Just like the inability to detect silica, water is also not Raman active, which makes it an especially good tool for determining species present in aqueous solutions.

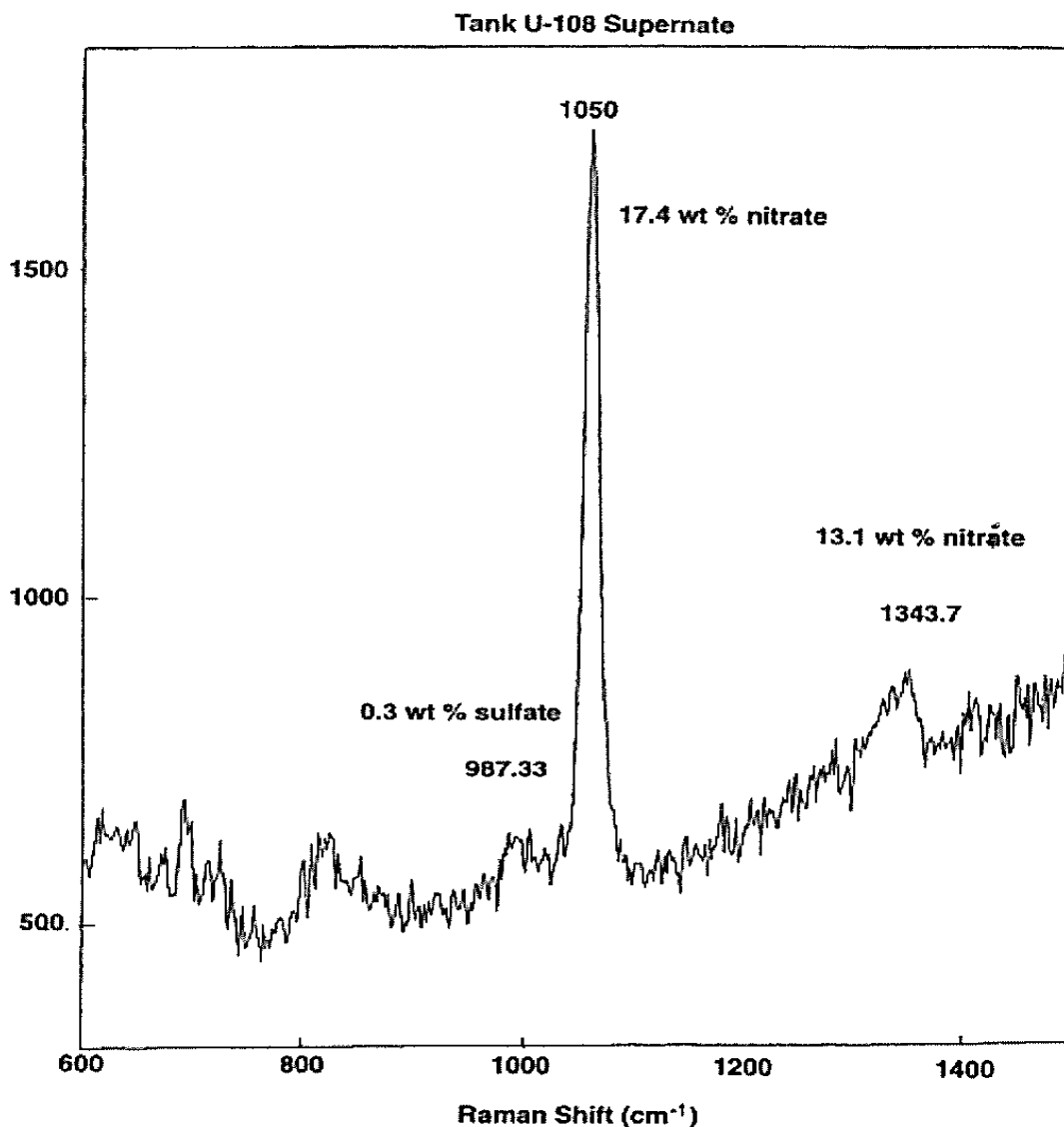


Figure 6: Tank U-108 supernate containing multiple ions in solution such as sulfate, nitrate and nitrite [3].

Another application of Raman spectroscopy that is of particular effectiveness when opaque containers are encountered is Spatially Offset Raman Spectroscopy (SORS). SORS has been used by homeland security for detection of explosives in solutions stored in opaque containers [4]. Figure 7 specifically illustrates how SORS is more effective at analyzing the contents of a container over that of conventional Raman (CR) spectroscopy. The top four spectra provide the fingerprint of a given suntan lotion and the resulting spectra with SORS and CR as well as the Raman spectra of the container alone. SORS produces a spectrum that matches that of the lotion, while CR mainly sees the spectrum of the container. The lower four spectra show the same container with 30 % hydrogen peroxide. Again SORS was able to analyze the contents while ignoring the container and detected the hydrogen peroxide (explosive material) that was being investigated. This demonstrates the ability of SORS to provide information on containerized unknown liquids without having to open the container.

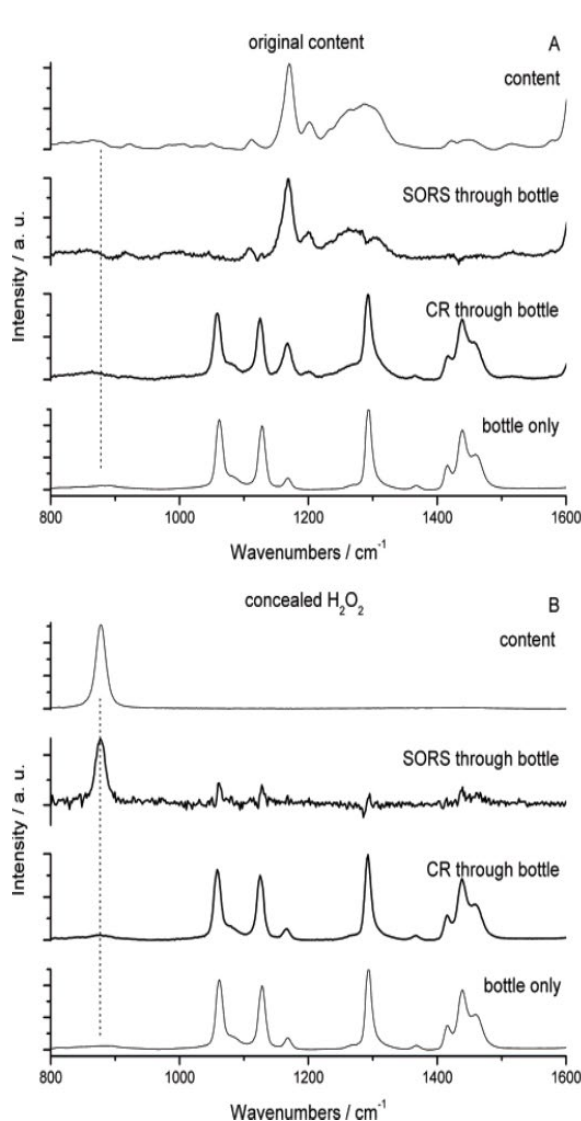


Figure 7: A comparison of conventional Raman and Offset Raman illustrates that ability to determine hydrogen peroxide in a yellow colored container of suntan lotion.

SORS is available in a handheld form in the Agilent Resolve Handheld Through-Barrier Identification System (Figure 8). The Resolve instrument is for hazardous material identification and as such is designed for use by technicians in cumbersome personal protective equipment (PPE) and should be relatively simple to operate within a glovebox. The Resolve instrument is capable of both conventional and spatially offset Raman.



Figure 8: Agilent Resolve Handheld Through-Barrier Identification System [5].

B. Testing of Surrogate Waste Samples

The LANL DWT prepared test samples intended to act as surrogates for waste that might be seen in site cleanup projects. The samples were sent to the vendor Federal Resources for Raman and FTIR analysis with the Thermo Scientific™ Gemini™ instrument (Figure 9). The samples reported here are Surrogate A, Surrogate Soil, Surrogate Sludge, and magnesium nitrate hexahydrate. These surrogate samples consisted of a solid (a sorbent, soil, or sludge) mixed with 10 wt. % magnesium nitrate hexahydrate. Surrogate A was made with the sorbent Aquaset II, and the Surrogate Soil and Surrogate Sludge samples were made with standard sandy soil (CRM-SA-C) and domestic sludge (CRM-S-D), respectively, procured from High Purity Standards (Table 2).



Figure 9: Thermo Scientific™ Gemini™ combined FTIR and Raman instrument [6].

Table 2: Contents of surrogate samples.

| Surrogate A | Surrogate Soil | Surrogate Sludge |
|--|--|--|
| Aquaset II: 4.81 g | Standard Sandy Soil: 10.84 g | Domestic Sludge: 4.30 g |
| Mg(NO ₃) ₂ ·6H ₂ O: 0.52 g | Mg(NO ₃) ₂ ·6H ₂ O: 1.08 g | Mg(NO ₃) ₂ ·6H ₂ O: 0.43 g |

The Thermo Scientific™ Gemini™ handheld analyzer is a two in one unit that can perform both FTIR and Raman analysis of solids and liquids. The instrument was designed for use in the field by military forces and first responders and as such is certified to military standards for survivability and it was designed to be operated by technicians in extensive PPE. For example, it has a resistive touchscreen which can be operated with gloved fingers. The sample interface for FTIR on the Gemini™ is diamond crystal attenuated total reflectance (ATR) window, and the Raman has a fiber optic probe that can be aimed at the sample, or directed into a small sample chamber.

Figures Figure 10 and Figure 11 show the output spectra from the Gemini™ instrument of the FTIR and Raman analysis of the pure magnesium nitrate hexahydrate, respectively. The instrument was able to produce clear spectra of the sample and the built-in library was

able to correctly identify it as magnesium nitrate hexahydrate in both the FTIR and Raman modes. While the Gemini™ is capable of analyzing the spectra of some mixtures, the interpretation will be limited to what is in the stored library. As such it was not surprising that it was not able to analyze the spectra of the more complex surrogate samples and identify the contents. Figure 12, Figure 14, and Figure 16 contain the output FTIR spectra produced by the Gemini™ instrument for the Surrogate A, Surrogate Soil, and Surrogate Sludge samples, respectively. It can be seen that the three different samples produced similar, but still unique FTIR spectra. This demonstrates the ability of FTIR to produce spectra that could potentially help group unknown materials in individual waste drums together.

Figure 13, Figure 15, and Figure 17 contain overlays of the FTIR spectra of the surrogate samples with that of magnesium nitrate hexahydrate. These were produced by copying the raw spectral data (.spc files) from the Gemini™ instrument and opening them in spectral analysis software [7] where the spectra were normalized to 1 and smoothed with a moving average smoothing function (please note that since the spectra were normalized they do not provide an indication of the intensity of the signal seen by the instrument). This data was then exported to Microsoft™ Excel™ and graphed. These overlays demonstrate how FTIR can be used to help identify potential constituents of unknown samples. In Figure 13 a sharp peak is seen around 1650 cm^{-1} in the magnesium nitrate hexahydrate spectra, and a similar but less intense peak in the Surrogate A spectra. This is in the region where one would expect to see the N-O stretch absorption band. Aquaset II, used to make Surrogate A, is a Sepiolite clay mineral which is a complex magnesium silicate. In the FTIR spectra of Surrogate A the peaks observed in the region around 1000 cm^{-1} are characteristic of silicate IR absorption bands [8]. The broad absorption band seen in the $3000\text{--}3700\text{ cm}^{-1}$ range of both spectra is characteristic of O-H stretching and as such is a strong indicator for the presence of water, which is known to be in the samples from the hydrates associated with the magnesium nitrate. Similar interpretations can be made of the overlays in Figure 15 and Figure 17 where there are peaks characteristic of nitrate, silicate, and water. Such interpretations will need to be made by a trained subject matter expert as matrix effects can slightly shift where absorption bands appear. This can be observed in the nitrate absorption band in Figure 17 as the Surrogate Sludge spectrum appears to have two peaks in the region. This could be due to a different metal nitrate salt being present in the sludge resulting in a slightly shifted N-O absorption band. Such determinations can be made by properly trained personnel and demonstrate the great deal of chemical and structural information that FTIR spectra can provide.

Figure 18 and Figure 20 show the Raman spectra generated by the Gemini™ instrument for the Surrogate A and Surrogate Sludge samples, respectively. The Raman results on the samples we prepared were not as successful as the FTIR results. This was due to excessive fluorescence generated in some of the samples from the excitation laser, potentially a result of high amounts of metal oxides in the samples. As such a Raman spectrum was not generated for the Surrogate Soil sample, and Figure 17 is an example of when fluorescence is an issue but a spectrum could still be produced. In Figure 17 the fluorescent band is seen as very broad, and peaks are appearing as sudden drops in Raman scattering intensity

instead of sudden increases. Fluorescence issues can be mitigated by tuning the wavelength of the excitation laser to one that does not generate the fluorescence, however this solution is not generally applicable to handheld instruments. This is why pairing Raman with FTIR, as is the case with the Gemini™ instrument, is such a powerful combination for in-field analysis. Each technique covers for the weaknesses of the other. When fluorescence prevents Raman analysis, a FTIR spectrum will likely be able to be produced. And while FTIR has difficulty analyzing aqueous solutions or even samples where there is just some water present due to the strong O-H IR absorption bands, water does not have a strong Raman interaction and therefore Raman can easily analyze the contents of aqueous samples.

A Raman spectrum was obtained for the Surrogate A sample (Figure 18) and as such an overlay of the Raman spectra of Surrogate A and the pure magnesium nitrate hexahydrate could be produced (Figure 19). These Raman spectra went through the same normalization and smoothing process as the FTIR spectra. In Figure 19 a sharp peak is observed in the 1000-1100 cm^{-1} region of the pure magnesium nitrate hexahydrate spectra. This is the characteristic peak of the nitrate ion, and it will shift slightly depending on the counterion it is paired with and the sample matrix. This effect can be seen in the spectra of Surrogate A. There is a weak peak near 1100 cm^{-1} in the Surrogate A spectra, and we would expect a weaker nitrate peak as the magnesium nitrate hexahydrate was only 10 wt. % of the sample. The nitrate peak is slightly shifted from the nitrate peak in the pure sample, which could be expected from the significantly different sample matrix generated by the 90 wt. % Sepiolite present in the sample. While the Raman spectra were not as robust as the FTIR spectra generated from the surrogate samples, the Raman results of Surrogate A do corroborate the interpretation of the FTIR results of Surrogate A. This kind of corroboration between the different techniques will be very useful when it comes to analyzing the results of unknown materials, as it will provide additional evidence to support the interpretation of the trained subject matter expert.

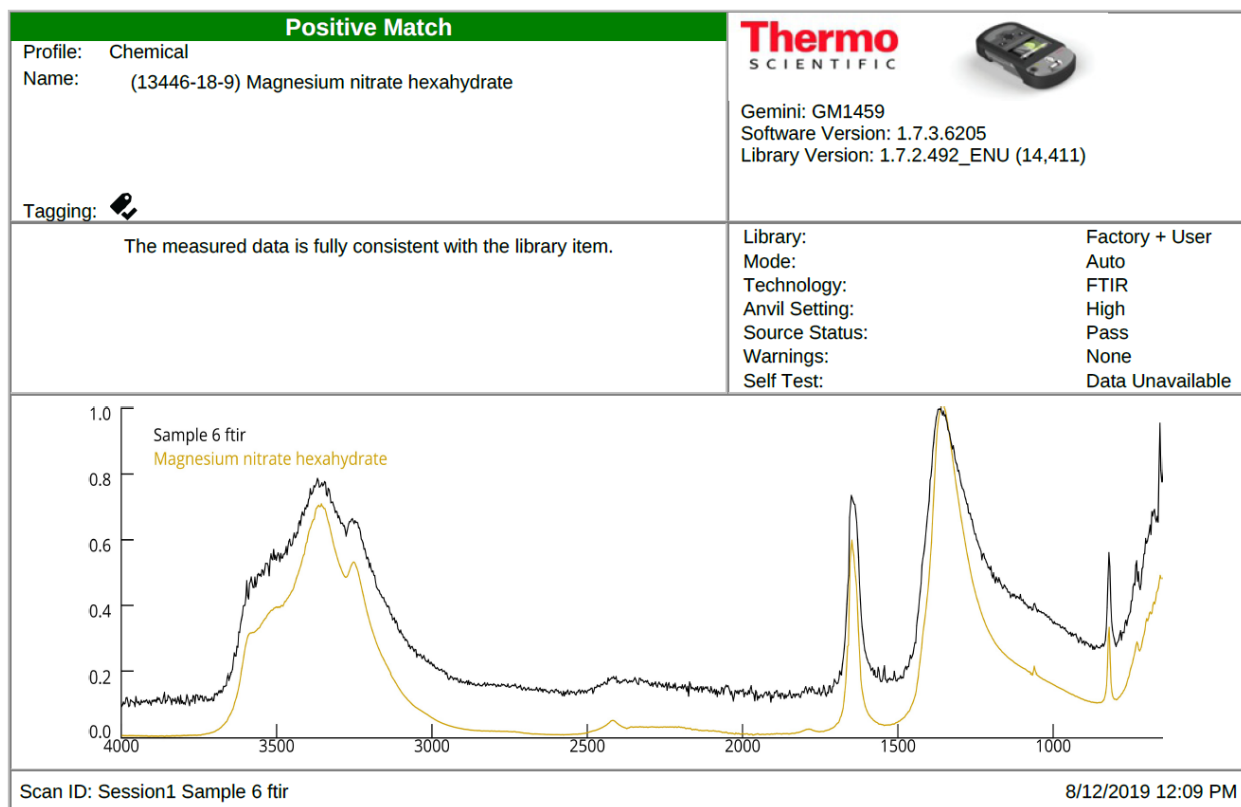


Figure 10: Output FTIR spectra of magnesium nitrate hexahydrate from the Gemini™ instrument.

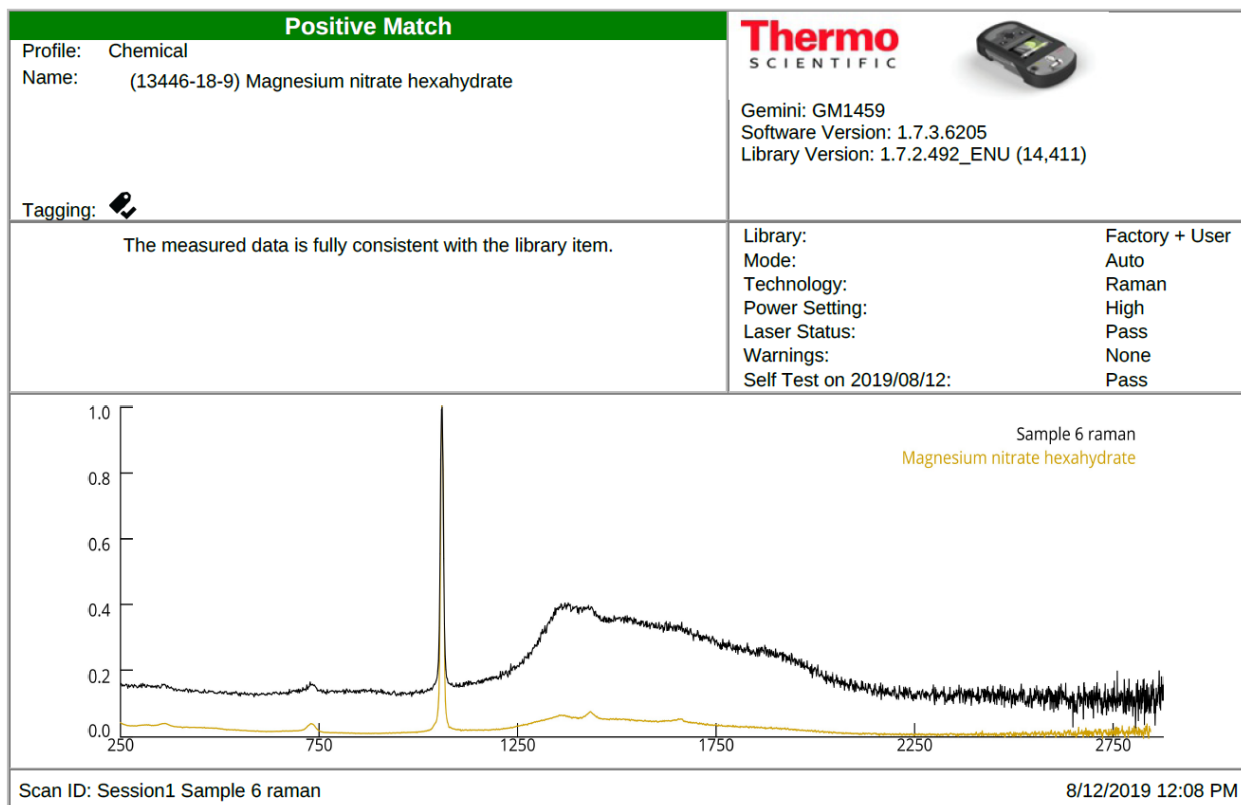


Figure 11: Output Raman spectra of magnesium nitrate hexahydrate from the Gemini™ instrument.

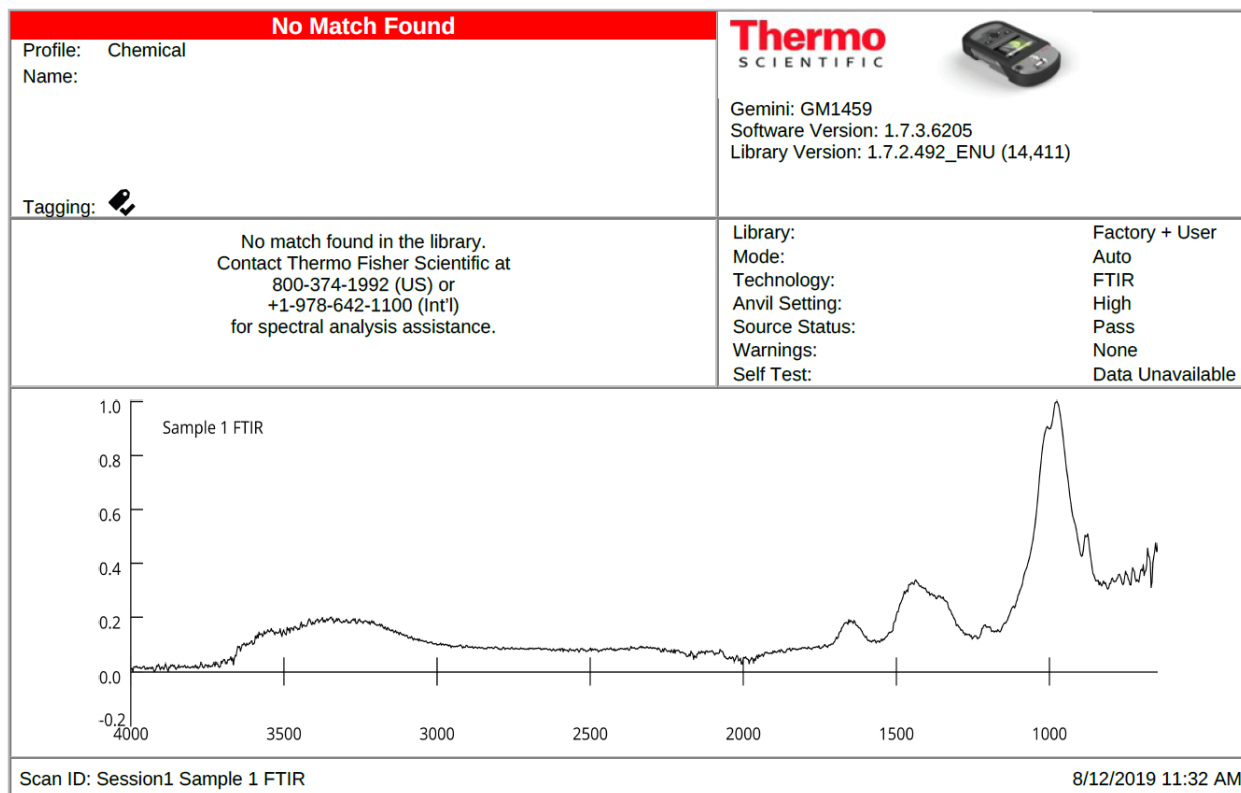


Figure 12: Output FTIR spectra of Surrogate A from the Gemini™ instrument.

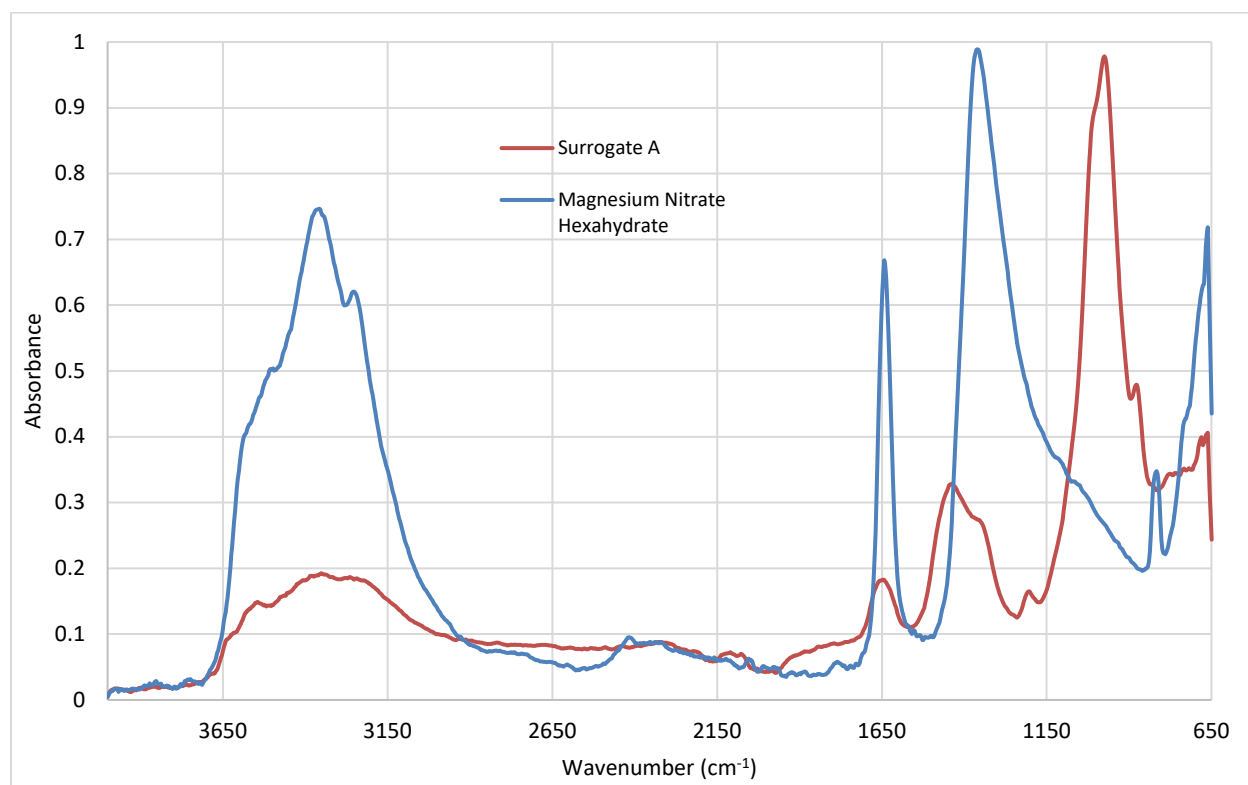


Figure 13: FTIR spectra overlay of Surrogate A and magnesium nitrate hexahydrate.

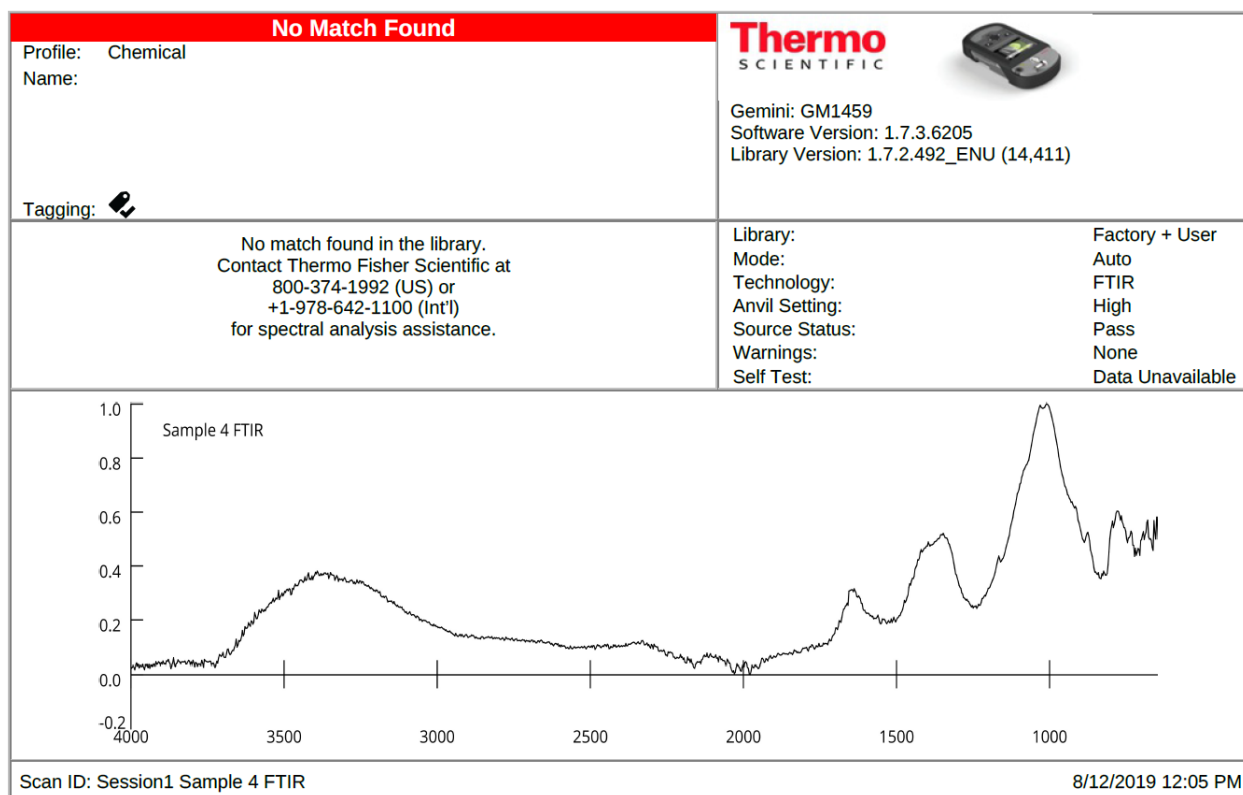


Figure 14: Output FTIR spectra of Surrogate Soil from the Gemini™ instrument.

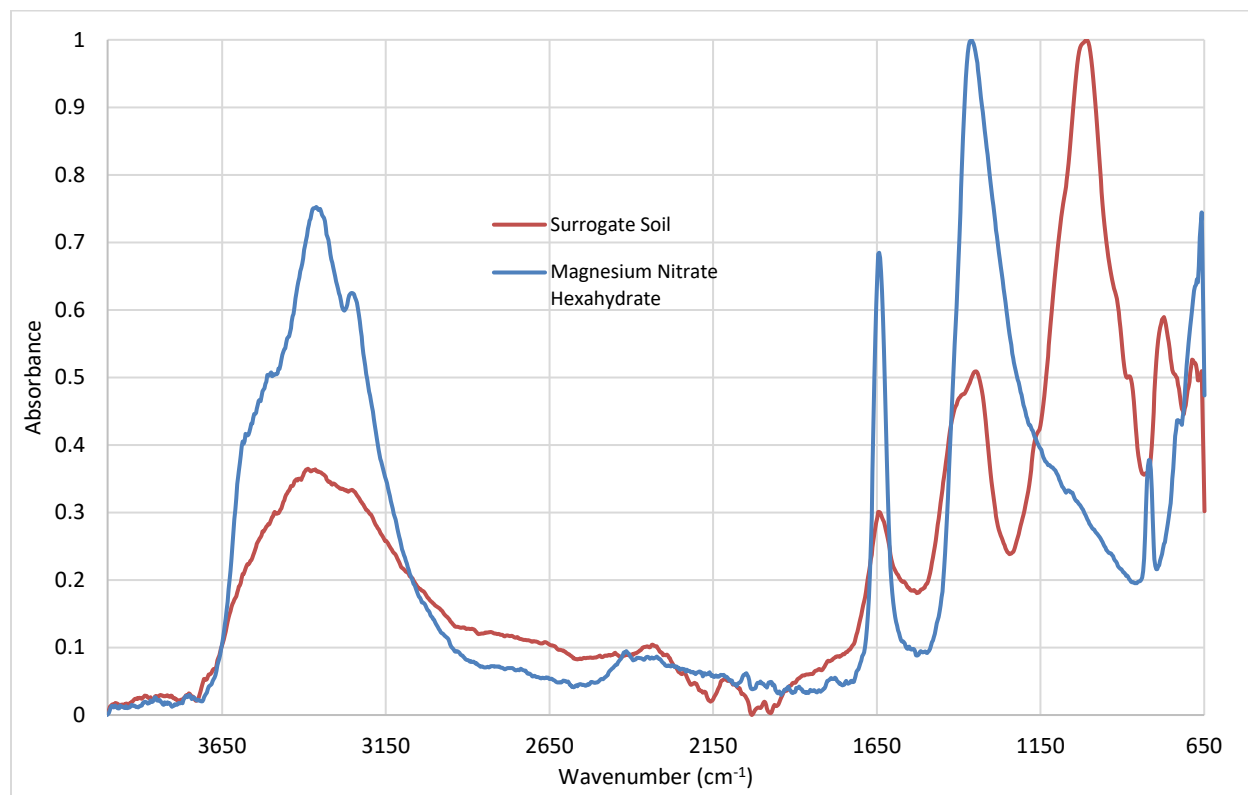


Figure 15: FTIR spectra overlay of Surrogate Soil and magnesium nitrate hexahydrate.

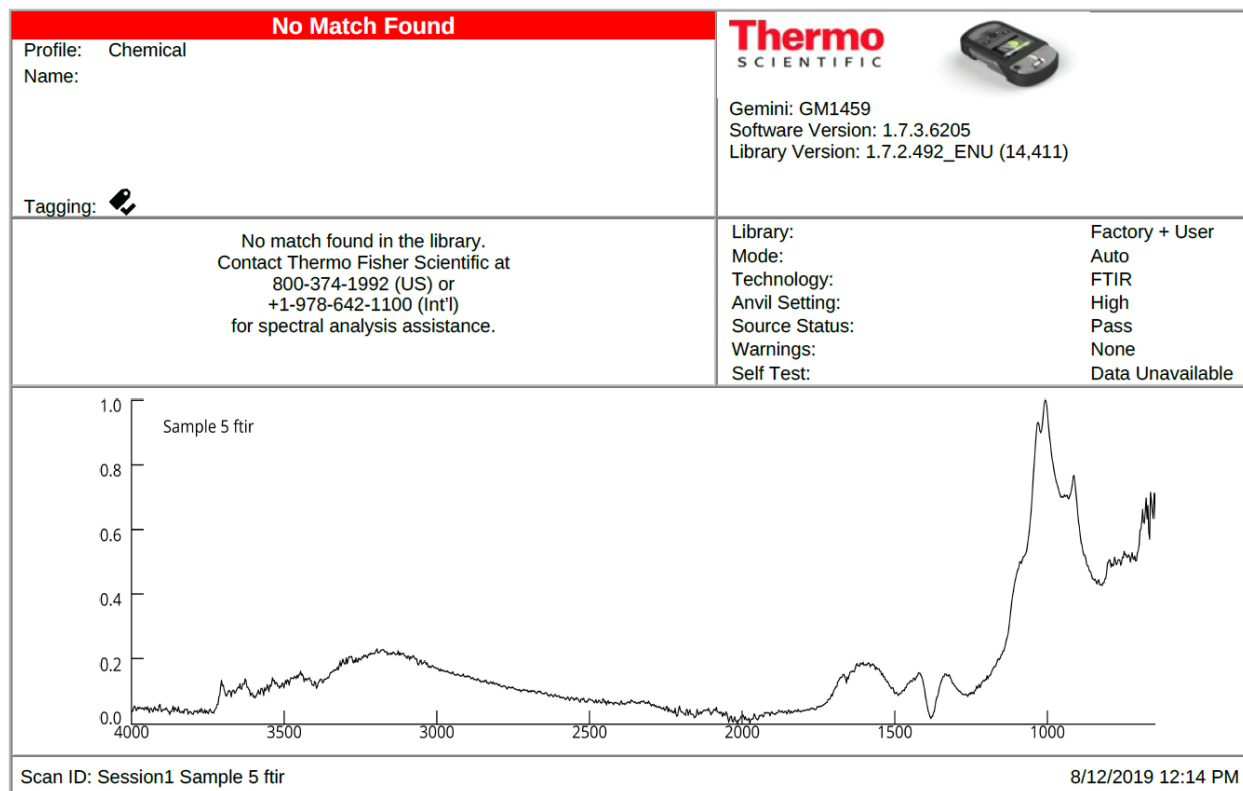
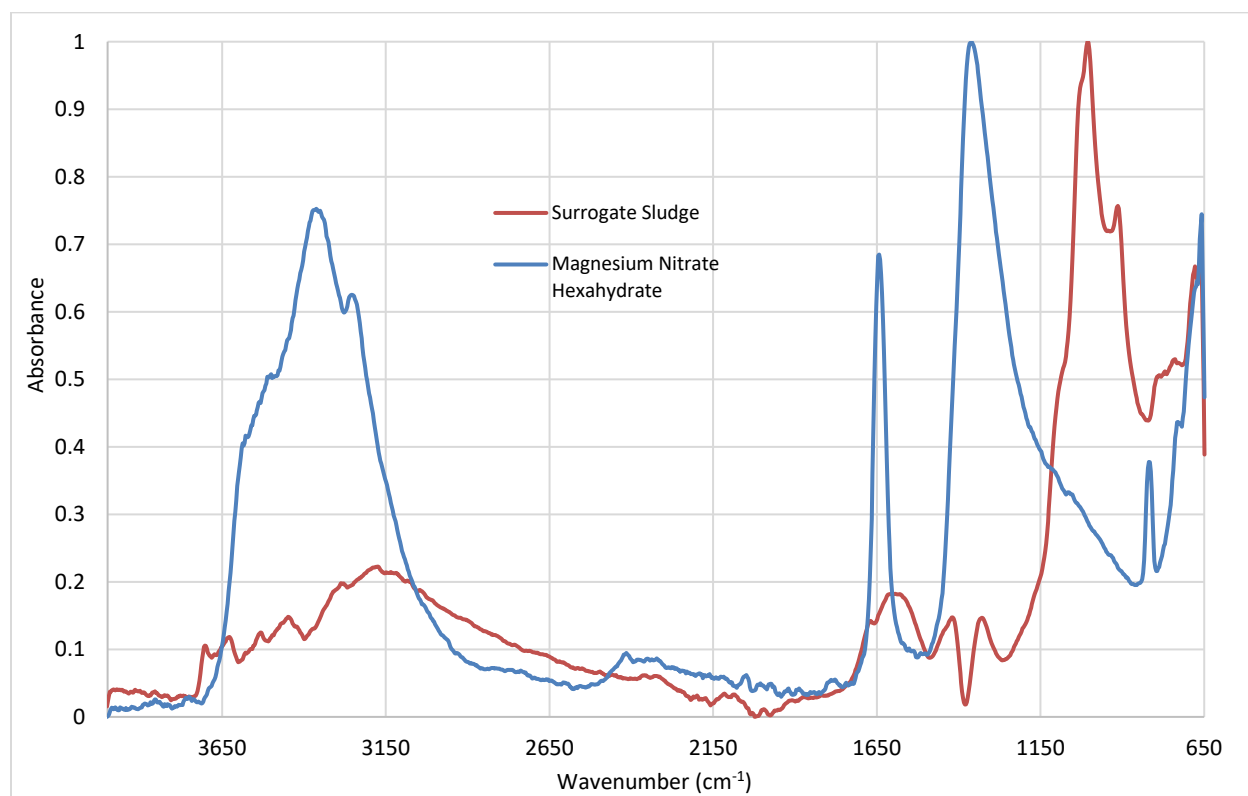


Figure 16: Output FTIR spectra of Surrogate Sludge from the Gemini™ instrument.



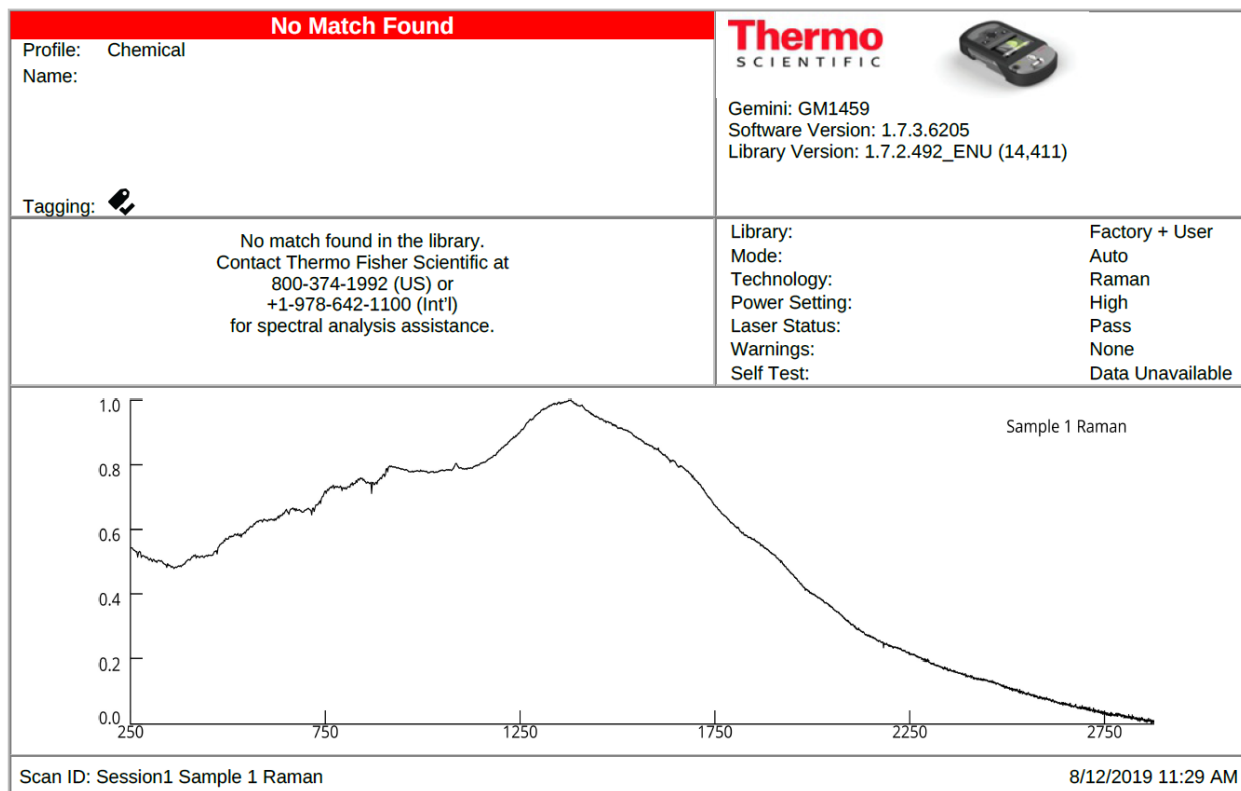


Figure 18: Output Raman spectra of Surrogate A from the Gemini™ instrument.

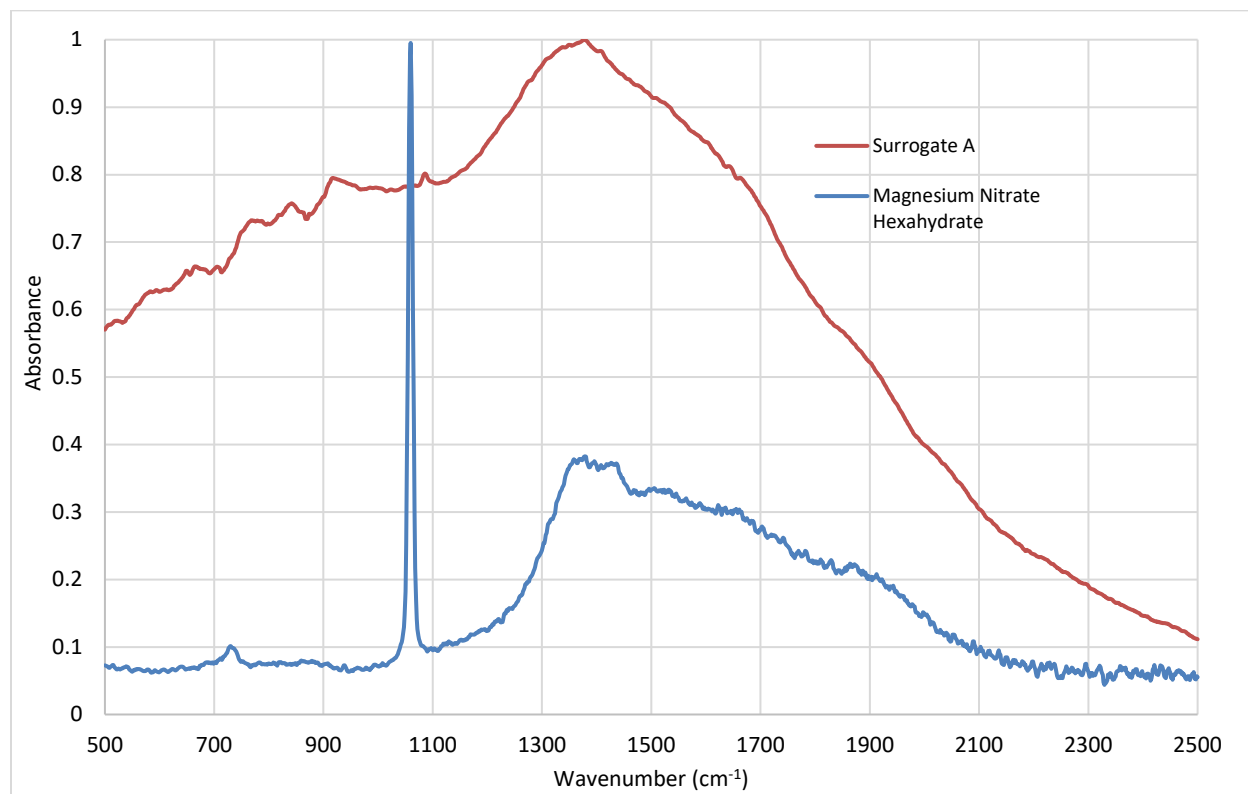


Figure 19: Raman spectra Overlay of Surrogate A and magnesium nitrate hexahydrate.

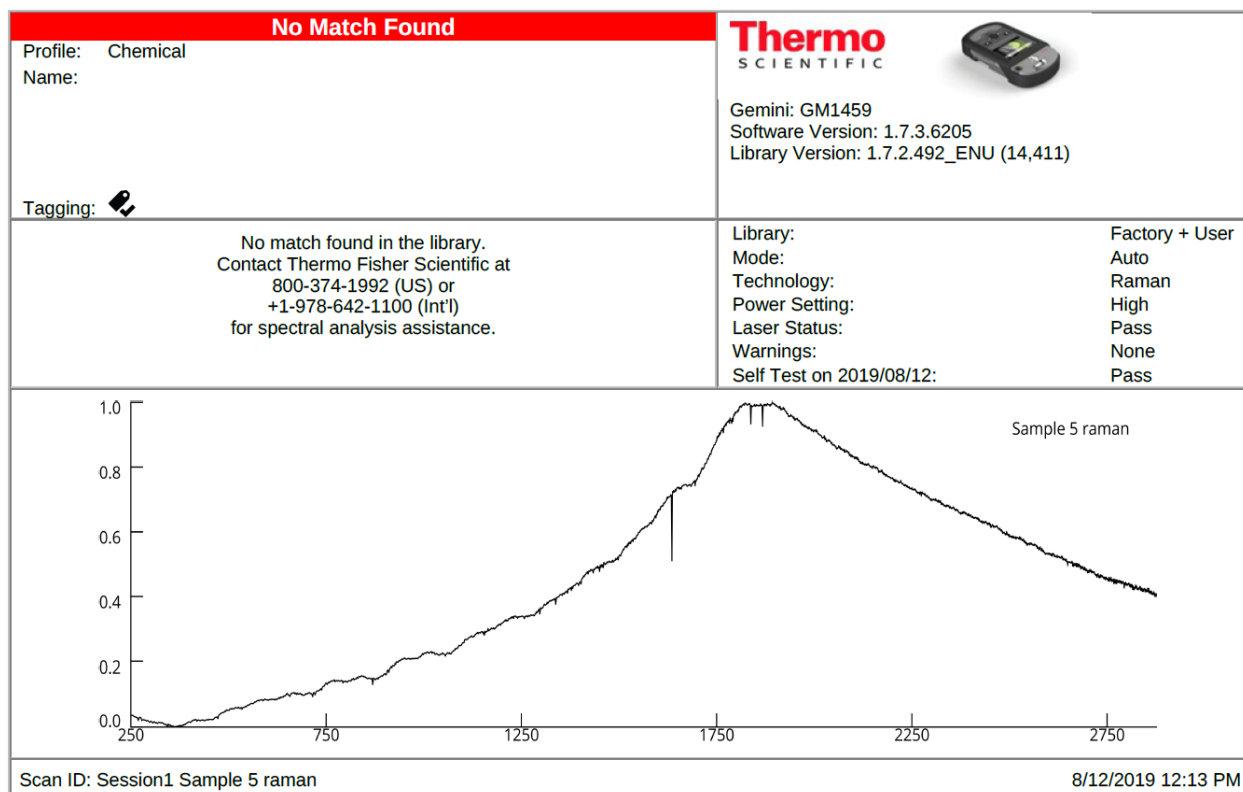


Figure 20: Output Raman spectra of Surrogate Sludge from the Gemini™ instrument.

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Attachment B: Laser Induced Breakdown Spectroscopy (LIBS)

Jef Lucchini (LANL DWT)

LIBS has been used for more than 30 years as a laboratory technique, capable of analyzing any element in the periodic table [1]. Recently, the technique has been miniaturized into a handheld device capable of analyzing any element, depending on the spectrometer range chosen for the device. Handheld LIBS instruments have been successfully used in many fields (mining, environment, archaeology, forensics, etc.) [2], including nuclear waste [3]. We expect that they could also be used for elemental characterization of radioactive wastes, such as homogeneous solids.

Many well-established spectroscopy companies (Bruker, Hitachi, SciAps, etc.) offer portable LIBS instruments of approximately equivalent performance and capability. The LANL DWT attended a few demonstrations of their top-of-the-line LIBS instruments, we focus on the Z-300 LIBS Analyzer from SciAps (Figure 21).



Figure 21: Handheld Z-300 LIBS Analyzer from SciAps [1].

A. Technique

LIBS operates by using a pulsed, focused laser and one or more spectrometers. A diagram of the technique is provided in Figure 22. A pulsed laser beam, typically in the 5-6 millijoules (mJ) per pulse energy range and pulsing 50 times per second (50 Hz) is fired at a sample. The laser beam passes through a lens, so it focuses down to approximately a 50 microns (μm) diameter. The pulse duration is 1-2 nanoseconds (ns), thus yielding a high power density to vaporize the material. Bound atomic electrons are stripped from the atoms comprising the material, and a plasma is produced around the area struck. As the plasma cools over a few hundred micro-seconds, the electrons recombine with the atoms, and in the process, emit light in the ultraviolet (UV), visible and IR spectrum. A portion of the emitted light is collected through lenses, and directed to a spectrometer. The spectrometer analyzes the emitted light by measuring the wavelength and the intensity of the light at specific wavelengths. An on-board software package compares the spectral lines with known characteristic wavelengths to identify the presence of elements, and uses the intensity of those lines with a recorded calibration, to quantify the concentration of the elements.

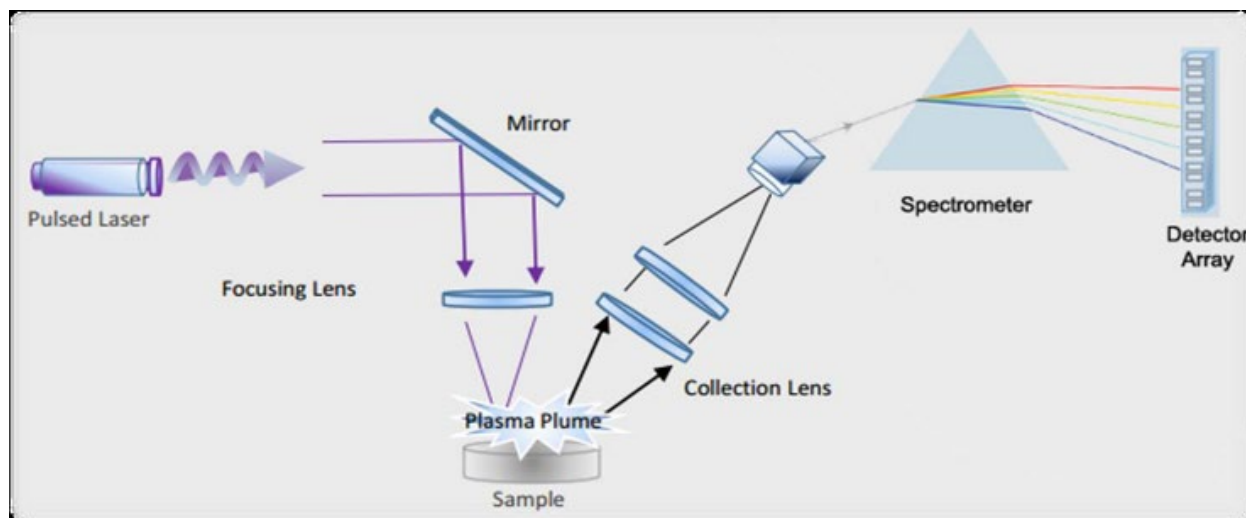


Figure 22: Diagram of the LIBS technique [4].

B. Capability, Performance and Advantages

Table 3 describes the capability, performance and advantages of the SciAps Z-300 handheld LIBS instrument. A few of these technical assets can be found in similar instruments from competitors.

Table 3: Assets of the SciAps Z-300 handheld LIBS instrument [5].

| | | |
|----|---|--|
| 1 | Analysis of every element in the periodic table of the elements | The broad spectral range from 190 nm to 950 nm yield wavelength coverage for entire periodic table of the elements. Qualitative, and quantitative (with proper calibration), measurement of elements of $Z \geq 1$ (from H to U). See Figure 23. |
| 2 | Air atmosphere, or argon purge to boost detection | Detection limits are typically parts per million (ppm) in a 10 second (s) measurement. An on-board, user-replaceable argon purge can improve the signal strength by ten times, particularly for emissions in the deep ultraviolet. Users may run the instrument in air atmosphere if the testing requires less precision, or if restrictions on gas canisters exist. Note that each argon canister provides high precision analysis for approximately 600 burns. Connection of the instrument to a standard stationary argon tank is possible. |
| 3 | Light, small and fast | Weight is 4 pounds (lbs) with battery. Dimensions are 8.25" x 11.5" x 4.5". Results are shown in 1 s, full test time is 3 s. |
| 4 | Laser beam rastering (proprietary technology) | Because testing a single location may not average out inhomogeneities, and the laser beam may hit an inclusion or embedded contaminant, the instrument rasters the laser beam to different discrete positions and automatically averages the results. A rastered laser provides the best LIBS precision possible. The users may setup their own raster pattern. |
| 5 | Spatial mapping at a micron-scale | The laser spot size is approximately 50 μm in diameter. The instrument has an integrated XY stage, plus a Z-direction focus adjustment, which provides the ability to generate a spatial grid on the sample surface. The laser raster capability patterns up to a 16 x 16 grid, which is equivalent to 256 locations. |
| 6 | Depth profiling | No sample grinding is needed. The instrument can fire 10 (or more) surface cleaning shots in 0.2 s to burn away surface contaminants, dirt, etc. The cleaning shot capability may also be used for depth profiling (1-100 μm), for example, monitoring elemental concentrations as a function of sample thickness. |
| 7 | Solid samples analyzed as is, or pelletized powders | Any solid materials can be analyzed as is: powders, loose soil samples, pressed/pelletized materials (Figure 24). The use of excipients or binding agents for pressed samples is optional. |
| 8 | Specific Apps available | The instrument is supplied with specific built-in apps, such as for soils, ores, alloys. A complete software package provides the users with the ability to choose their own elements, emission lines, create intensity ratios, and produce their own calibration curves. See Section B for two specific applications of interest for waste characterization. |
| 9 | Daily maintenance | Daily maintenance consists of the following two actions (at minimum): cleaning the blast shield (to remove the dust that builds up overtime on the quartz blast shield, preventing optimal light collection), and performing an automated calibration when required. |
| 10 | Laser Class 3b to 1 | The instrument has a Class 3b laser. However, because of a sample sensor on-board, operation can be run under Class 1 conditions (subject to local Laser Safety Officer approval only). No laser safety glasses are typically required. |
| 11 | On-board camera, WiFi, Bluetooth, USB connections | An on-board camera allows the user to visualize the surface to analyze with a spatial precision of 50 μm . WiFi, Bluetooth and USB connections are available capabilities to transfer acquired data. |

B1. Two Specific Apps of Interest

Many programs (called apps by SciAps) are included in the SciAps Z-300 unit for specific applications: Alloy, Geochem (for mining), Environmental, etc. Two apps, described below, are of particular interest for waste characterization.



- The Empirical App and the ProfileBuilder software combined allow the user to develop a calibration curve, save it to the analyzer, and utilize it later for immediate quantitative results on unknown materials. To develop a specific calibration curve, the user may enter assays of known materials for calibration, locate elemental lines after testing samples, calculate intensities and intensity ratios, and perform spectral overlays, baseline subtractions and smoothing.
- The ElementPro App is designed for qualitative testing. Any samples can be tested, and no calibrations are needed. After a few seconds of acquiring the data, the spectra are automatically examined. Using the proprietary library of LIBS emission lines (provided by the manufacturer), relative emission strengths are built for the entire periodic table of the elements, and they are compared to the experimental peaks. Elements that have a high probability of being present in the sample, because most or all of their emission lines were detected, are identified, and their relative abundance in the sample is estimated.

B2.Demonstrations of Performance on Soil and Sludge

The LANL DWT provided SciAps five samples of soil and sludge for analysis using a Z-300 unit and the on-board ElementPro App. The samples were standard sandy soil and domestic sludge, procured from High Purity Standards (Table 4), and three mixtures of those. The elemental composition of the two standard products is known, and documented in the certificates of analysis. The elemental composition (or assay) of each of the three mixtures was calculated using the weight of each standard used in the preparation of the mixtures. Measurements of the five samples of soil and sludge were carried out by SciAps technician using a Z-300 unit. Some results are presented herein.

Table 4: Soil and Sludge standards from High Purity Standards and used in this study.

| Category | Name of the product | High Purity Standards Part number |
|------------|---------------------|-----------------------------------|
| Sandy soil | Sand-spiked-level C | CRM-SA-C |
| Sludge | Domestic sludge | CRM-S-D |

• Detection of Beryllium

Because beryllium carbide can generate significant amounts of methane when heated in the presence of acid, base, or water, it was identified as a reactant in a secondary chemical reaction, responsible for dislodging the lid and ejecting the contents of drums in the ARP V drum event in Idaho in April 2018 [6]. Therefore, it is important to determine the presence of this metal in a waste drum. A major “characterization” technique used in the Idaho Cleanup Project (ICP) is VE. However, the presence of beryllium is not visually recognizable

in wastes that are beryllium-contaminated. Other techniques are therefore needed to detect beryllium, and LIBS is being considered [7].

The standard samples of soil and sludge chosen in this work are representative materials of homogeneous solids found in the Idaho waste (because of their physical texture – powders-, and their major elemental composition). They contain minute amounts of beryllium: 6 ppm and 1 ppm for the standard soil and sludge respectively. The standard samples of soil and sludge were pelletized (Figure 24), and analyzed using a SciAps Z-300 instrument and the on-board ElementPro App. On the experimental spectra shown in Figure 25, a main emission peak for beryllium clearly appears at 313 nm. Beryllium can be measured in homogeneous solids using handheld LIBS, in concentrations as low as 1 ppm.

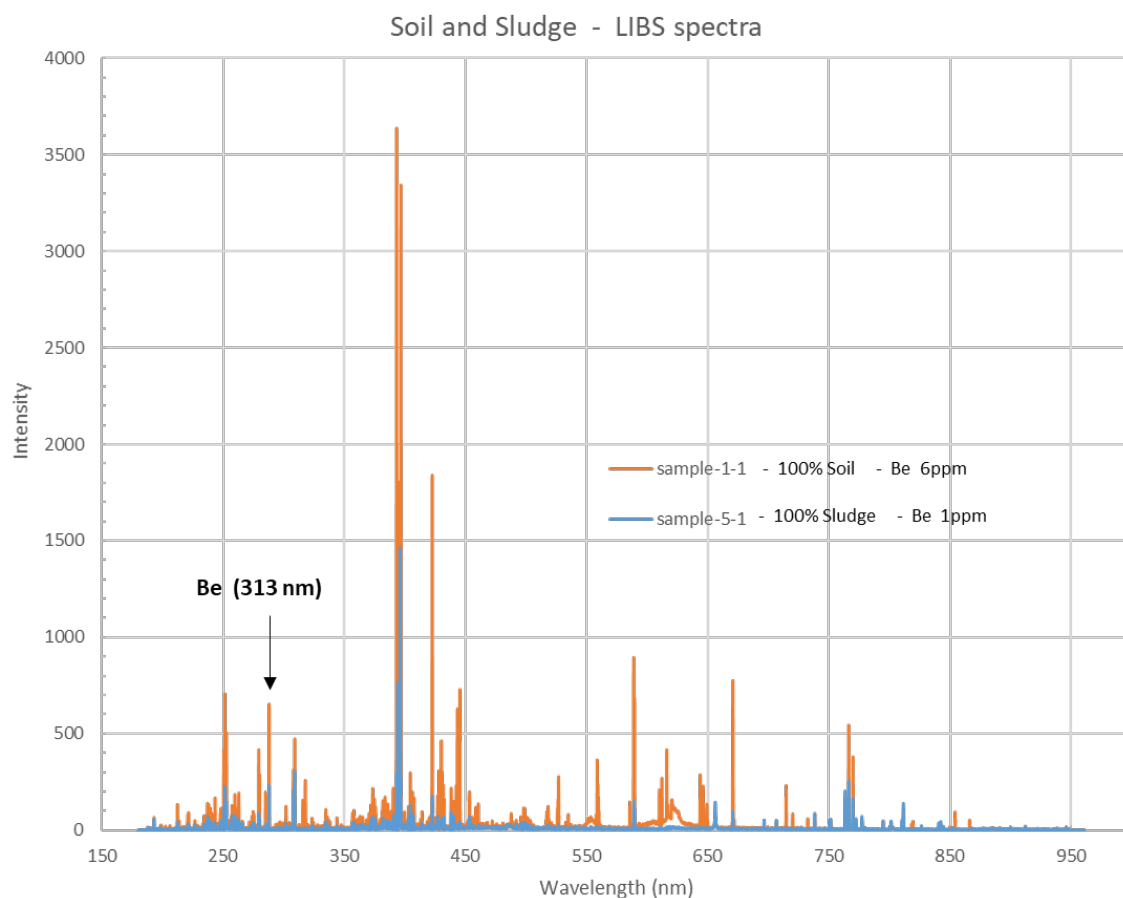


Figure 25: LIBS spectra of pelletized standard soil (sample 1-1) and sludge (sample 5-1). The peak of beryllium appears at 313 nm.

- **Powder vs. Pellet**

Homogeneous solid waste can be compacted or loosened (i.e., in a powder form) in the field. The elemental characterization technique is efficient and accurate on both types of materials.

Sample #3 (50 wt. % of standard soil, and 50 wt. % of standard sludge) was tested as a powder using a SciAps Z-300 instrument and the on-board ElementPro App. A video of this test is included (Video 1). This video document shows that a handheld LIBS instrument can be used on loose materials.

Video 1: Measurement of Sample #3 (powder form).



Video Apr 25, 11 36 29 AM.mov

When using the proper instrumental settings (minimal number of shots, minimal acquisition time, etc.), the qualitative results on powder materials can be meaningful. In Table 5, the calculated elemental composition of Sample #3 (in wt. %) is displayed. Green shaded cells indicate the elements that were detected using a LIBS Z-300 and the SciAps ElementPro App on powder of Sample #3. The results are accurate, with the exception of iron that was not measured by the instrument. The fact that iron was missed in the experimental test is more likely due to overlapping emission lines from different elements, and because of a low limit of detection (LOD) typical in loose samples.

Table 5: Calculated composition of Sample #3 (in wt. %). Green shaded cells indicate the elements that were detected using a LIBS Z-300 and the SciAps ElementPro App on powder of Sample #3.

| Sample 3 | |
|---------------------|--------|
| Composition (wt. %) | |
| Al | 66% |
| Ca | 7% |
| Fe | 22% |
| K | 1% |
| Mg | 1% |
| Mn | 1% |
| Na | 1% |
| P | 0% |
| S | 0% |
| Ti | 0% |
| Be | 0.003% |
| Ba | 0% |
| Cr | 0% |
| Zn | 0% |
| Li | |

With loose or unpressed soils, LIBS results versus assays are generally scattered due to the lack of sample homogeneity and density. Denser the sample is, bigger the plasma is, and therefore, more signal is generated, and a better LOD is obtained. SciAps reports that LODs are about 3 to 4 times higher for loose soil samples (testing on the ground) compared to alloys [8]. For example, a LOD of 15-20 ppm can usually be expected for beryllium in unpressed soil [8]. This level of detection would however exceed any requirements for beryllium measurement in TRU radioactive waste to be shipped to WIPP.

- **Demonstration of a Measurement, and Cleaning of the Instrument**

Video 2 gives an example of a typical measurement of a pressed sample using a SciAps Z-300 instrument with default manufacturer settings, and the on-board ElementPro App. Video 2 also shows the first steps of cleaning the instrument.

Video 2: Measurement of Sample #4 (pressed powder), and demonstration of a typical cleaning of the instrument.



Video Apr 25, 11 43 12 AM.mov

The measurement shown in Video 2 was performed on Sample #4, which was made of 25 wt. % of standard soil and 75 wt. % of standard sludge. The spectra and results of the measurement are displayed in Figure 26 and Table 6 respectively. The major elemental constituents were identified by the instrument (green shaded cells in Table 6). Despite a very low amount of beryllium in the sample (0.002 wt. %), a peak shows up at 313 nm in Figure 26, which could be traced back to beryllium if making the proper adjustments to the measurement settings. The results of this measurement demonstrate that a complex, solid and compact sample can be characterized accurately and rapidly in situ using a handheld LIBS instrument.

A handheld LIBS instrument requires relatively minimum care in order to maintain optimum conditions for measurements. As shown at the end of Video 2, the operator needs to make sure the quartz blast shield stays clean and free of dust, so that the collection of light from the plasma is maximum (see item 9 in Table 3). Every so often (particularly when shooting at powders) the blast shield needs to be removed using a screwdriver, and the tip of the instrument and the quartz shield need to be cleaned using a compressed air can, for example. This maintenance steps should be implementable in a glove box environment, such as the Drum Packaging Station (DPS) in Idaho.

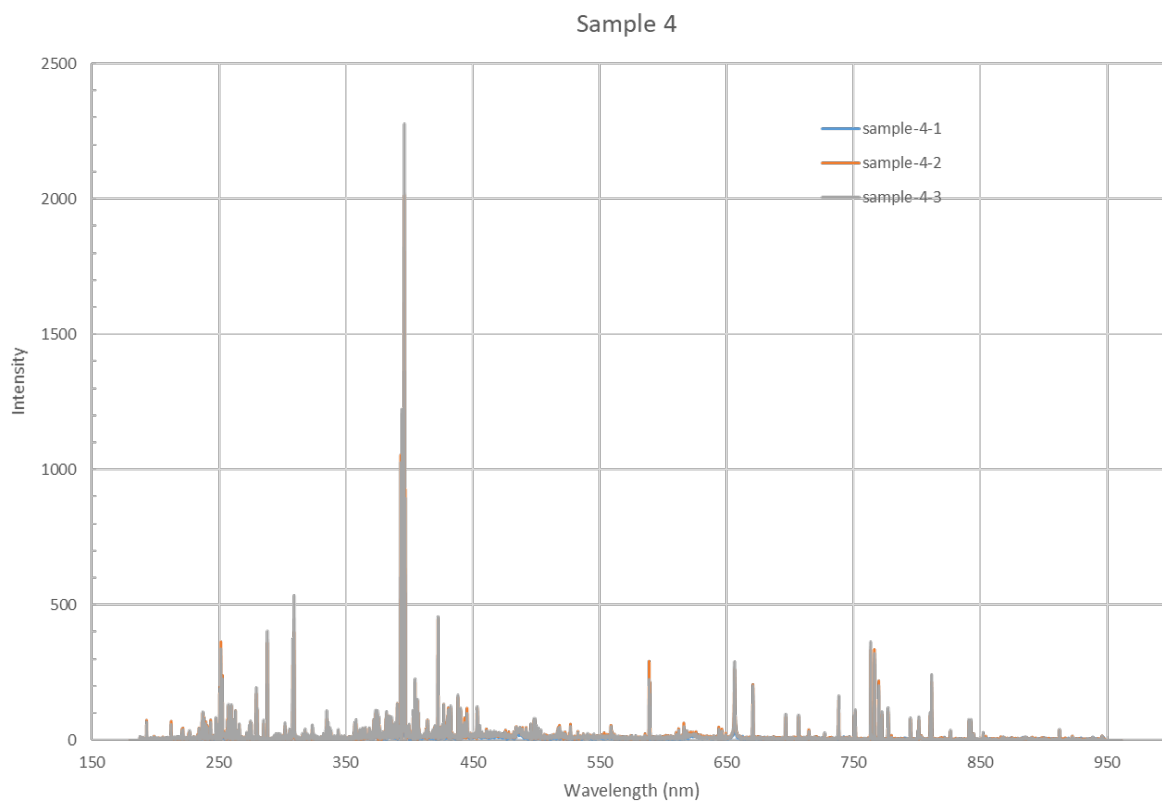


Figure 26: LIBS spectra of compressed Sample #4.

Table 6: Calculated composition of Sample #4 (in wt. %). Green shaded cells indicate the elements that were detected using a LIBS Z-300 and the SciAps ElementPro App on compressed Sample #4.

| Sample 4 | |
|---------------------|--------|
| Composition (wt. %) | |
| Al | 73% |
| Ca | 3% |
| Fe | 19% |
| K | 1% |
| Mg | 1% |
| Mn | 1% |
| Na | 1% |
| P | 0% |
| S | 0% |
| Ti | 1% |
| Be | 0.002% |
| Ba | 0% |
| Cr | 0% |
| Zn | 0% |
| Si | |

C. Potential Use of Handheld LIBS in the Idaho Cleanup Project

There is a high potential for the use of a portable LIBS instrument to characterize the remaining TRU waste to be treated in the ICP. Particularly, most of the waste to be processed in the SRP area constitutes of unknowns, with very limited or no AK documentation. The current characterization methods used in Idaho (VE, non-destructive assay, real-time radiography) appear insufficient to meet the WIPP Waste Acceptance Criteria (WAC) in terms of compliance and safety. In this document, we have shown that a portable LIBS instrument can deliver in-situ and instantaneously accurate and reliable information on the elemental composition of solid waste (powders included). Therefore, we are recommending its use to acquire and augment the current knowledge of the SRP waste (Table 7).

Table 7: Suggested conditions for the use of a handheld LIBS instrument (e.g., SciAps Z-300) in the ICP SRP waste.

| | |
|-------------------|--|
| Location | Drum packaging station (DPS) |
| Storage | In a protective pocket on the inside wall of the DPS |
| Use | On unknown waste materials for non-certified characterization |
| Type of analysis | Qualitative (ElementPro App) |
| Targeted elements | Be, C, U (to potentially identify comingled Be ₂ C and U) |
| | Zr, Ca (potential pyrophorics) |
| | Na, N, O (potential presence of nitrate or nitric acid) |

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